Constant-Potential Reactions Simultaneously Controlled by Charge-transfer and Mass-transfer Polarization at Planar, Spherical and Cylindrical Electrodes

Charles A. Johnson and Sidney Barnartt

Edgar C. Bain Laboratory
For Fundamental Research
United States Steel Corporation
Research Center
Monroeville, Pennsylvania

In general the rate of an electrode reaction will be determined by both charge-transfer and mass-transfer polarization, even in the case of slow reactions if the concentration of one reactant is small. The purpose of this paper is to examine the theoretical time behavior of the reaction rate at constant potential, for electrodes having planar, spherical or cylindrical symmetry. The electrochemical systems considered will be limited to first-order charge-transfer mechanisms. The current-time relation for planar electrodes at constant potential is known. This will be examined in greater detail, particularly from the standpoint of rapid reactions. Then a general solution will be given in closed form for spherical electrodes. Finally an approximate solution will be developed for cylindrical electrodes, and a numerical method for the general solution outlined.

Current-potential relations

The current-potential relation for a reaction of the type: $R^{(z-n)+} = O^{z+} + ne^-$ was derived by Gerischer:[1]

$$i/i_o = \frac{a_R}{a_R^o} \exp\left[(1-\beta)n\varepsilon\eta\right] - \frac{a_O}{a_O^o} \exp\left[-\beta n\varepsilon\eta\right] \tag{1}$$

Here i is the net anodic current density at overpotential η, i_o the exchange current density, β the transfer coefficient and $\varepsilon \equiv F/RT$. The activities of R and O are designated a_R and a_O at the electrode-solution interface at time t; these differ from the bulk values a_R^o and a_O^o as a result of mass transfer effects. Equation 1 is limited to those charge-transfer mechanisms in which all of the electrical work involved occurs during the rate-determining step, and which are first order (defined at constant potential) with respect to the activities a_R and a_O.[2,3]

For rapid reactions the following approximation to eq. 1, also due to Gerischer,[4] is generally used,[5-7]

$$i/i_o = n\varepsilon\eta + \frac{a_R}{a_R^o} - \frac{a_O}{a_O^o} = n\varepsilon\eta + \frac{\Delta a_R}{a_R^o} - \frac{\Delta a_O}{a_O^o} \tag{2}$$

where $\Delta a_R = a_R - a_R^0$ and $\Delta a_O = a_O - a_O^0$. Equation 2 was derived on the assumption that η, Δa_R and Δa_O are all small, a set of limitations too confining for rapid reactions where activity changes develop rapidly. We propose, instead, a more basic relation for rapid reactions, valid at all values of Δa_R and Δa_O. This is obtained from eq. 1 by use of exp $(k\eta) \simeq 1 + k\eta$:

$$(i/i_o)_{\eta \to o} \simeq n\varepsilon\eta \frac{a_R}{a_R^0} + (1-\beta n\varepsilon\eta) \left(\frac{a_R}{a_R^0} - \frac{a_O}{a_O^0}\right) \tag{3}$$

where $\left(\dfrac{\Delta a_R}{a_R^0} - \dfrac{\Delta a_O}{a_O^0}\right)$ may be substituted for the last factor. Equation 3 reduces to

eq. 2 only if the assumption is made that Δa_R and Δa_O are small. This assumption is valid only during a very short interval after a rapid reaction is initiated; at longer times eq. 2 will exhibit greater deviations from the true relation (eq 1) than will eq. 3. An illustration of these deviations will be given below for the case of linear diffusion.

Planar electrodes
Potentiostatic current-time relations

Gerischer and Vielstich[8] have derived the solution, in closed form, for a first-order reaction described by eq. 1, with semi-infinite linear diffusion as the sole mass-transfer process. The electrolyte is assumed to contain excess neutral salt, so that concentration ratios may replace the activity ratios in eq. 1 with little error. The solution will be reproduced here and applied numerically to a typical fast reaction to illustrate the range of validity for eq. 2 and 3. The solutions for the concentrations and current density at the electrode surface are:

$$c_R = c_R^0 - \left(A/\lambda\kappa^{\frac{1}{2}}\right)\left[1 - \exp(\lambda^2 t)\mathrm{erfc}(\lambda t^{\frac{1}{2}})\right] \tag{4}$$

$$c_O = c_O^0 + (A/\lambda)\left[1 - \exp(\lambda^2 t)\mathrm{erfc}(\lambda t^{\frac{1}{2}})\right] \tag{5}$$

$$i = i_{(t=o)} \exp(\lambda^2 t)\mathrm{erfc}(\lambda t^{\frac{1}{2}}) \tag{6}$$

where the desired charge-transfer current corresponding to overpotential η is

$$i_{(t=o)} = i_o\left[\exp(1-\beta)n\varepsilon\eta - \exp(-\beta n\varepsilon\eta)\right] \tag{7}$$

Here the quantities λ and A are defined by

$$\lambda = \frac{i_o \exp[(1-\beta)n\epsilon\eta]}{nFc_R^o D_R^{\frac{1}{2}}} + \frac{i_o \exp(-\beta n\epsilon\eta)}{nFc_O^o D_O^{\frac{1}{2}}} \tag{8}$$

$$A = \frac{\kappa^{\frac{1}{2}} i_o \exp[(1-\beta)n\epsilon\eta]}{nFD_R^{\frac{1}{2}}} - \frac{i_o \exp(-\beta n\epsilon\eta)}{nFD_O^{\frac{1}{2}}} \tag{9}$$

with $\kappa \equiv D_R/D_O$, the ratio of the diffusion coefficients. It should be noted that the equations as given in the Gerischer-Vielstich paper[8] contained two errors (no post-publication correction found): (1) omission of $\kappa^{\frac{1}{2}}$ from the first term of A; (2) the quantity $(\kappa^{-\frac{1}{2}}A/\lambda)$ in eq. 4 was given as $(\kappa^{\frac{1}{2}}A/\lambda)$. The quantity A may be written in terms of the charge-transfer current as

$$A = i_{(t=0)} \left[nFD_O^{\frac{1}{2}} \right]^{-1} \tag{9a}$$

Substituting for A in eq. 4 and 5 one obtains the concentrations in terms of the charge-transfer current:

$$c_R = c_R^o - i_{(t=0)} \left[nFD_R^{\frac{1}{2}}\lambda \right]^{-1} \left[1 - \exp(\lambda^2 t)\,\mathrm{erfc}(\lambda t^{\frac{1}{2}}) \right] \tag{4a}$$

$$c_O = c_O^o + i_{(t=0)} \left[nFD_O^{\frac{1}{2}}\lambda \right]^{-1} \left[1 - \exp(\lambda^2 t)\,\mathrm{erfc}(\lambda t^{\frac{1}{2}}) \right] \tag{5a}$$

If the electrode reaction is rapid (η small), the current-time relation is still given by eq. 6 but the parameters $i_{(t=0)}$, λ and A may be simplified to:

$$i_{(t=0)} = i_o n\epsilon\eta \tag{10}$$

$$\lambda = \frac{i_o}{F} \left[\frac{\epsilon\eta}{c_R^o D_R^{\frac{1}{2}}} + \left(\frac{1}{n} - \beta\epsilon\eta \right) \left(\frac{1}{c_R^o D_R^{\frac{1}{2}}} + \frac{1}{c_O^o D_O^{\frac{1}{2}}} \right) \right] \tag{11}$$

$$A = i_o \eta / RT\, D_O^{\frac{1}{2}} \tag{12}$$

The current-time relation (eq. 6) is obtainable from eq. 1 by substitution for c_R and c_O from eq. 4 and 5. Similarly, substitution for these concentrations in eq. 2 and 3 yields the corresponding approximate current-time curves. The following numerical case was selected to illustrate the deviations of the approximate curves from the rigorous one: $i_o = 5 \times 10^{-3}$ A/cm^2 at 25°C, $\beta = 0.5$, $n = 1$, $c_O^0 = 5 \times 10^{-2}$ and $c_R^0 = 10^{-2}$ mole/l; $D_O = 2 \times 10^{-5}$ and $D_R = 10^{-5}$ cm^2/s. With these values the reaction rates should be roughly equivalent to those reported[9] for the ferrous-ferric reaction on bright platinum. Figure 1 shows the calculated current-time curves for an applied overpotential of 10 mV. At the longest time shown ($t = 0.21$ s) c_O has changed by 2.4% and c_R 17%. These changes are sufficient to cause considerable deviation of eq. 2 from the true curve, but eq. 3 remains extremely close. Thus eq. 3 should be used as the basic rapid-reaction equation, while the former is an approximation useful only for very short reaction times.

It may be noted from eq. 4a, 5a that the maximum change in concentration, which occurs at $t \to \infty$ (and $i \to 0$), is given for each of the diffusing substances by $i_{(t=o)} \left[nFD^{\frac{1}{2}}\lambda \right]^{-1}$. At any given time t the same fraction $\left[1 - \exp(\lambda^2 t)\mathrm{erfc}(\lambda t^{\frac{1}{2}}) \right]$ of the maximum change has taken place for each substance. In the present example this fraction is 0.572 at the longest time considered (0.21 second).

Evaluation of $i_{(t=o)}$ and λ.

If the argument $\lambda t^{\frac{1}{2}}$ is small eq. 6 may be approximated by

$$i = i_{(t=o)} \left[1 - (2/\pi^{\frac{1}{2}}) \lambda t^{\frac{1}{2}} + \lambda^2 t \right] \tag{13}$$

For a very short period, up to the time the last term in brackets ceases to be negligible, the initial region of the i-$t^{\frac{1}{2}}$ curve is linear (e.g. $t<10$ ms in Fig. 1). From this line $i_{(t=o)}$ may be obtained by extrapolation, and the slope of the line yields λ. Experimentally, however, this linear region will often be inaccessible for moderately rapid reactions with present-day potentiostatic circuitry. An appreciable time is required to attain the control potential within a small fraction of a millivolt (η being small), primarily because it is necessary to incorporate automatic compensation for the IR drop between the controlled electrode and the capillary tip of the reference electrode[10].

To permit analysis of experimental current-time curves which exclude the initial linear region, we present here another simple procedure for evaluating $i_{(t=o)}$ and λ. In this method one selects an arbitrary time t, and reads the current from the experimental curve at times t and 4t. The ratio of these two currents is

$$\frac{i_{(t)}}{i_{(4t)}} = \frac{\exp(\lambda^2 t)\mathrm{erfc}(\lambda t^{\frac{1}{2}})}{\exp(4\lambda^2 t)\mathrm{erfc}(2\lambda t^{\frac{1}{2}})} \tag{14}$$

This ratio is readily calculated for all values of $\lambda t^{\frac{1}{2}}$ from tables[11] of the function $\exp(y^2)\mathrm{erfc}(y)$, and is shown in Fig. 2 for $\lambda t^{\frac{1}{2}} = 0$ to 1. The experi-

mental value of the current ratio for a specific time t_1 has a corresponding value of $\lambda t_1^{\frac{1}{2}}$ which is obtained from Fig. 2, and this value yields λ. The procedure may be repeated for times $t_2, t_3, t_4 \ldots$ to obtain a mean value of λ. Utilizing the mean λ, each measured current at $t_1, t_2, t_3 \ldots$ yields $i_{(t=0)}$ from eq. 6. If the deviations of the individual values of λ or of $i_{(t=0)}$ about the mean value are found to be small and randomly distributed, one has support for the a priori assumption of a first-order charge-transfer mechanism. As $\lambda t^{\frac{1}{2}}$ increases, the slope of the curve in Fig. 2 decreases; hence the precision with which λ can be evaluated decreases with increasing time in the intermediate-time range $(0.85 \gtrsim i_{(t)}/i_{(t=0)} \gtrsim 0.45)$ [16].

Evaluation of charge-transfer parameters [6,7]

For slow electrode reactions (η relatively large), it is sufficient to determine $i_{(t=0)}$ from potentiostatic current-time curves as a function of η, either for anodic (η positive) or cathodic (η negative) polarization. The well-known Tafel plot then yields both i_0 and β. For rapid reactions (small η), measurement of $i_{(t=0)}$ in a given solution yields i_0 from eq. 10; since i_0 is given by

$$i_0 = i_{0,s} \ (a_R^0)^\beta \ (a_O^0)^{1-\beta} \tag{15}$$

where $i_{0,s}$ is the standard exchange current density,[12] β is obtained from determinations of i_0 with solutions in which a_R^0 is varied at constant a_O^0, or a_O^0 varied at constant a_R^0.

Evaluation of D_R or D_O

The ratio $i_{(t=0)}/\lambda$ from eq. 7 and 8 is given by

$$\frac{i_{(t=0)}}{\lambda} = nF \left[\exp(n\epsilon\eta) - 1 \right] \left[\frac{\exp(n\epsilon\eta)}{c_R^0 \sqrt{D_R}} + \frac{1}{c_O^0 \sqrt{D_O}} \right]^{-1} \tag{16}$$

and is seen to be independent of i_0 and β. Thus the values of $i_{(t=0)}$ and λ obtained from a single potentiostatic current-time curve permit estimation of one of the diffusion coefficients if the other is known. This is so even though $i_{(t=0)}$ and λ are obtained from the current-time curve at short times, where the reaction is partly controlled by the charge-transfer kinetics.

The current at long times ($\lambda t^{\frac{1}{2}} \gg 1$) is under complete mass-transfer control, and a plot of i vs. $t^{-\frac{1}{2}}$ is linear with a slope proportional to the ratio $i_{(t=0)}/\lambda$, as was shown by Gerischer and Vielstich.[8] Hence the long-time currents permit evaluation of the diffusion coefficient somewhat more directly.

Spherical Electrodes

The problem is solved here in closed form for an electrode reaction at constant potential involving a first-order charge-transfer mechanism (eq 1), with diffusion in a system of spherical symmetry as the sole mode of mass transfer. The mathematical formulation of the problem comprises differential equations:

$$D_R \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_R}{\partial r} \right) = \frac{\partial c_R}{\partial t} \ , \quad D_O \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_O}{\partial r} \right) = \frac{\partial c_O}{\partial t}$$

with initial conditions $(t=0, r \geq a)$: $c_R = c_R^0$, $c_O = c_O^0$ and boundary conditions (all t):

$$r \rightarrow \infty: \qquad c_R \rightarrow c_R^0 \; ; \quad c_O \rightarrow c_O^0$$

$$r = a: \quad i = nFD_R \frac{\partial c_R}{\partial r} = - nFD_O \frac{\partial c_O}{\partial r}$$

Here $\underline{a}$ is the electrode radius, and $\underline{i}$ is the current density given by eq 1 with concentrations substituted for activities.

General Solution

The general solution of this problem, derived by the Laplace transform method, is presented in the Appendix. Equations A17 and A18 give the concentration changes at the electrode, and eq A19 the current density. Two regions of the current-time curve are of particular interest for extracting the charge-transfer parameters, namely the initial short-time section and the final long-time section.

(a) Short-time solution: This is obtained by use of the approximation, $\exp x^2 \operatorname{erfc} x \simeq 1 - (2/\pi^{\frac{1}{2}}) x + x^2$, which is valid for small x. Equations A17-19 convert to

$$c_R = c_R^0 - \frac{i_{(t=0)}}{nFD_R^{\frac{1}{2}}} \left[\frac{2}{\pi^{\frac{1}{2}}} t^{\frac{1}{2}} - \left(1 + \frac{D_R^{\frac{1}{2}}}{a\lambda} \right) \lambda t \right] \tag{17}$$

$$c_O = c_O^0 + \frac{i_{(t=0)}}{nFD_O^{\frac{1}{2}}} \left[\frac{2}{\pi^{\frac{1}{2}}} t^{\frac{1}{2}} - \left(1 + \frac{D_O^{\frac{1}{2}}}{a\lambda} \right) \lambda t \right] \tag{18}$$

$$i = i_{(t=0)} \left[1 - \frac{2}{\pi^{\frac{1}{2}}} \lambda t^{\frac{1}{2}} + \left(1 + \frac{\lambda_R D_R + \lambda_O D_O}{a\lambda^2} \right) \lambda^2 t \right] \tag{19}$$

where

$$\lambda_R = \frac{i_o \exp(1-\beta) n\varepsilon\eta}{nFD_R c_R^0} \quad ; \quad \lambda_O = \frac{i_o \exp(-\beta n\varepsilon\eta)}{nFD_O c_O^0} \tag{20}$$

and also $\lambda = \lambda_R D_R^{\frac{1}{2}} + \lambda_O D_O^{\frac{1}{2}}$ and $i_{(t=0)} = nF(\lambda_R D_R c_R^0 - \lambda_O D_O c_O^0)$ as for planar geometry. A comparison of eq 19 with the corresponding eq 13 for the planar case shows that, over sufficiently short times such that the term in t is negligible, the sphere and plate electrodes yield the same linear $i - t^{\frac{1}{2}}$ relation. The linear behavior terminates sooner for the small sphere, however, since the term in t is larger in eq 19 than in eq 13.

If this linear portion of the curve is experimentally accessible, the values of λ and $i_{(t=0)}$ obtained from it can be used to determine the charge-transfer parameters and one of the diffusion coefficients, as described above for planar electrodes. For moderately rapid reactions, if the initial portion is inaccessible charge-transfer parameters can be determined from the long-time portion of the curve as shown below.

(b) Long-time solution: Use is made of the approximation, $\exp x^2 \operatorname{erfc} x = \pi^{-\frac{1}{2}} x^{-1}$, valid for large values of x. Equations A17-19 become

$$c_R = c_R^o - \frac{i_{(t=o)}}{nF} \cdot \frac{a}{D_R(1 + a\lambda_R + a\lambda_O)} \left[1 + \frac{a\lambda_O(\kappa^{\frac{1}{2}} - 1)-1}{1 + a\lambda_R + a\lambda_O} \cdot \frac{a}{(D_R\pi t)^{\frac{1}{2}}} \right] \quad (21)$$

$$c_O = c_O^o + \frac{i_{(t=o)}}{nF} \cdot \frac{a}{D_O(1 + a\lambda_R + a\lambda_O)} \left[1 + \frac{a\lambda_R(\kappa^{-\frac{1}{2}} -1)-1}{1 + a\lambda_R + a\lambda_O} \cdot \frac{a}{(D_O\pi t)^{\frac{1}{2}}} \right] \quad (22)$$

$$i = \frac{i_{(t=o)}}{1 + a\lambda_R + a\lambda_O} \left[1 + \frac{a^2(\lambda_R/D_R^{\frac{1}{2}} + \lambda_O/D_O^{\frac{1}{2}})}{1 + a\lambda_R + a\lambda_O} \cdot \frac{1}{(\pi t)^{\frac{1}{2}}} \right] \quad (23)$$

A plot of i against $t^{-\frac{1}{2}}$ is a straight line, of form

$$i = i_{(t \to \infty)} + \sigma \, t^{-\frac{1}{2}} \quad (23a)$$

with intercept

$$i_{(t \to \infty)} = \frac{i_{(t=o)}}{1 + a\lambda_R + a\lambda_O} \quad (23b)$$

and slope

$$\sigma = \frac{a^2(\lambda_R/D_R^{\frac{1}{2}} + \lambda_O/D_O^{\frac{1}{2}}) \, i_{(t=o)}}{\pi^{\frac{1}{2}} (1 + a\lambda_R + a\lambda_O)^2} \quad (23c)$$

It may be recalled[15] that reversible reactions at spherical electrodes also exhibit a linear $i - t^{-\frac{1}{2}}$ curve at long times, but the intercept and slope are then quite different from the corresponding expressions for irreversible reactions (eq 23b,c).

At long times the current at a spherical electrode goes towards the finite value given by eq 23b, whereas at a plane electrode the corresponding current goes to zero. In the latter case the reaction becomes essentially diffusion controlled[8] at $\lambda t^{\frac{1}{2}} > 1$ (or at $i/i_{(t=o)} < 0.43$), so that current measurements at long times give no information about the charge-transfer mechanism. With small spherical electrodes, however, the reaction remains under partial charge-transfer control at all times. Provided the diffusion coefficients are known, the charge-transfer parameters may be derived as follows. We define the quantity

$$\rho = \frac{\lambda_R}{\lambda_O} = \frac{c_O^o \, D_O}{c_R^o \, D_R} \exp(n\varepsilon\eta) \quad (24)$$

The combination of eq 23b, 23c and 24 yields

$$\frac{1}{\lambda_0} = a \left[-\frac{a \, i_{(t \to \infty)}}{\sigma \pi^{\frac{1}{2}}} \left(\frac{\rho}{D_R^{\frac{1}{2}}} + \frac{1}{D_O^{\frac{1}{2}}} \right) - \rho - 1 \right] \tag{25}$$

This permits evaluation of λ_0 corresponding to the value of η which establishes the current-time curve. After measuring current-time curves at several values of η, we may plot log λ_0 against η, since from eq 20

$$\log \lambda_0 \quad \log(i_0/nFD_O c_O^O) - (\beta n \varepsilon/2.3) \eta \tag{20a}$$

to obtain β from the slope and i_0 from the intercept at $\eta = 0$.

Particular case: $D_R = D_O$
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It is of interest to examine the special case of $D_R = D_O = D$ which was treated by Shain, Martin and Ross.[14] The time variations of current density and concentrations at the electrode surface become, from eq A17-19,

$$c_R = c_R^O - \frac{i_{(t=o)}}{nFD^{\frac{1}{2}}\lambda(1 + \delta)} \left[1 - \exp((1 + \delta)^2 \lambda^2 t) \mathrm{erfc}((1 + \delta)\lambda t^{\frac{1}{2}}) \right] \tag{26}$$

$$c_O = c_O^O + \frac{i_{(t=o)}}{nFD^{\frac{1}{2}}\lambda(1 + \delta)} \left[1 - \exp((1 + \delta)^2 \lambda^2 t) \mathrm{erfc}((1 + \delta)\lambda t^{\frac{1}{2}}) \right] \tag{27}$$

$$\frac{i}{i_{(t=o)}} = \frac{\delta}{1 + \delta} + \frac{1}{1 + \delta} \left[\exp((1 + \delta)^2 \lambda^2 t) \mathrm{erfc}((1 + \delta)\lambda t^{\frac{1}{2}}) \right] \tag{28}$$

where $\delta = D^{\frac{1}{2}}/a\lambda$. Equation 28 is equivalent to the solution for the current previously given.[14]

The short-time current at $\lambda t^{\frac{1}{2}} \ll 1$ now becomes

$$i = i_{(t=o)} \left[1 - 2\pi^{-\frac{1}{2}}\lambda t^{\frac{1}{2}} + (1 + \delta)\lambda^2 t \right] \tag{29}$$

Thus from a single potentiostatic current-time curve the initial linear $i - t^{\frac{1}{2}}$ portion yields λ and $i_{(t=o)}$, from which the charge-transfer quantities β and i_0 are evaluated, and the ratio $i_{(t=o)}/\lambda$ gives the diffusion coefficient (eq 16).

If the initial portion of the curve is experimentally inaccessible, it is possible to derive the charge-transfer parameters from the currents at longer times provided the diffusion coefficient is known. Shain et al[14] described a treatment of the longer-time currents involving trial-and-error curve fitting; this treatment is restricted to slow reactions at relatively high η. We note here that the long-time current is given by eq 23, which when simplified for $D_R = D_O = D$ yields

$$\frac{i}{i_{(t=o)}} = \frac{\delta}{1 + \delta} + \left(\frac{1}{1 + \delta}\right)^2 \frac{1}{\pi^{\frac{1}{2}}\lambda t^{\frac{1}{2}}} \tag{30}$$

This provides a more direct method, and one which is applicable to rapid reactions. The slope σ and intercept $i_{(t \to \infty)}$ of this linear $i/t^{-\frac{1}{2}}$ relation yields λ in the form

$$\lambda = cD\pi^{\frac{1}{2}} (a^2 i_{(t \to \infty)} - a\sigma\pi^{\frac{1}{2}}D^{\frac{1}{2}})^{-1} \tag{31}$$

From λ the quantity $\delta = \sqrt{D}/a\lambda$ is calculated, whence $i_{(t=0)}$ is obtained from the intercept $i_{(t \to \infty)} = i_{(t=0)} \delta(1 + \delta)^{-1}$. We may determine $i_{(t=0)}$ in this way at several values of η, using a single solution and either anodic or cathodic polarization. Thus for anodic polarization the charge-transfer current is given by eq 7, which may be rearranged to

$$\log \left(\frac{i_{(t=0)}}{\exp(n\epsilon\eta) - 1} \right) = \log i_o - \left(\frac{\beta n\epsilon}{2.3} \right)\eta \tag{32}$$

A plot of the left side against η yields i_o (intercept) and β (slope).

Cylindrical Electrodes

Here the problem comprises a first-order charge-transfer mechanism (eq 1) combined with diffusion to a cylindrical electrode of radius a as the sole mass-transfer process. As before, the time variations of current and concentrations at the electrode surface are to be determined for a reaction at constant potential. The mathematical description consists of differential equations:

$$\frac{\partial c_R}{\partial t} = D_R \left[\frac{\partial^2 c_R}{\partial r^2} + \frac{1}{r}\frac{\partial c_R}{\partial r} \right] \quad ; \quad \frac{\partial c_O}{\partial t} = D_O \left[\frac{\partial^2 c_O}{\partial r^2} + \frac{1}{r}\frac{\partial c_O}{\partial r} \right]$$

with initial conditions ($t = 0$, $r \geq a$): $c_R = c_R^o$, $c_O = c_O^o$, and boundary conditions (all t):

$$r \to \infty: \qquad c_R \to c_R^o \qquad ; \qquad c_O \to c_O^o$$

$$r = a: \quad i = nFD_R \frac{\partial c_R}{\partial r} = -nFD_O \frac{\partial c_O}{\partial r}$$

A solution of this problem based on the use of Laplace transforms, is described in the Appendix. The method does not lead to a general solution in closed form, but the entire current-time curve may be determined numerically for any specific case. An approximate solution, valid at sufficiently short times, is derived with the use of asymptotic expansions. The current and the concentrations at the electrode surface are given by eq A33-35 of the Appendix. For the special case $D_R = D_O = D$, these equations convert to:

$$i/i_{(t=0)} = 1 - 2\pi^{-\frac{1}{2}}\lambda t^{\frac{1}{2}} + (1 + \delta/2)\lambda^2 t \tag{33}$$

$$c_R = c_R^o - \frac{i_{(t=0)}}{nFD^{\frac{1}{2}}} (2\pi^{-\frac{1}{2}}t^{\frac{1}{2}} - \bar{\lambda}t) \tag{34}$$

$$c_O = c_O^o + \frac{i_{(t=0)}}{nFD^{\frac{1}{2}}} (2\pi^{-\frac{1}{2}}t^{\frac{1}{2}} - \bar{\lambda}t) \tag{35}$$

where $\bar{\lambda} = \lambda(1 + \delta/2)$; quantities λ and δ are the same as defined above for planar and spherical symmetry. The equations reduce to the corresponding ones for planar electrodes if the cylinder is large ($a >> D^{\frac{1}{2}}/\lambda$). It is seen from eq 33 that there will be a short period of time during which a cylindrical electrode of any radius will yield the same linear $i - t^{\frac{1}{2}}$ relation as does the plane electrode. Deviation from this line, represented by the term in $\lambda^2 t$, will develop somewhat faster at a small cylindrical electrode than at a plate, but not so fast as at a spherical electrode of the same radius.

Comparison of planar, spherical and cylindrical electrodes

A numerical solution was carried out[13] (see Appendix) for the current-time curve at a small cylinder of radius $a = \sqrt{D/\lambda}$ (hence $\delta = 1$) for the special case of $D_R = D_O = D$. This is compared in Fig. 3 with the corresponding curve for a sphere of the same radius, obtained from eq 28. Also shown is the curve for a large sphere or large cylinder ($a >> \sqrt{D/\lambda}$), which is the same as eq 6 for the plane. At $\lambda t^{\frac{1}{2}} = 5$ the current ratio for this small sphere is close to the value $\delta/(1 + \delta) = \frac{1}{2}$ for $t \to \infty$ (see eq 28). The current ratio for the planar electrode goes to zero as $t \to \infty$. The curve for the cylinder is positioned about midway between the other two.

Figure 4 presents the short-time approximations to these curves, as given by eqs 13, 20 and 33 for the planar, spherical and cylindrical cases respectively. These approximate curves lie somewhat above the corresponding curves in Fig. 3, but for the range $\lambda t^{\frac{1}{2}} = 0$ to 0.25 the deviation is small. At $\lambda t^{\frac{1}{2}} = 0.25$ the currents given in Fig. 4 are 1.4% high for the planar electrode, 2.6% high for the cylindrical and 4.3% high for the spherical electrode.

As the electrode radius is increased above the value $\sqrt{D/\lambda}$, the upper two curves in Fig. 3 and 4 will move gradually closer to the planar-electrode curve.

Summary

1. A current-potential relation for rapid reactions, applicable to first-order charge-transfer mechanisms, is proposed and illustrated by a numerical example. This equation (eq 3) has a much wider range of validity than the form previously used (eq 2).

2. The analysis of potentiostatic current-time curves for planar electrodes, for reactions controlled simultaneously by charge-transfer and mass-transfer polarization, has been extended. This analysis is based upon measurements of the ratio of current at some time t to that at 4t, and permits extraction of the charge-transfer parameters β and i_o from the experimentally more accessible part of the curve following the linear $i - t^{\frac{1}{2}}$ portion.

3. Closed-form solutions to the general boundary-value problem for spherical electrodes are derived.

4. The boundary-value problem for cylindrical electrodes has been treated, and a general method for obtaining numerical solutions outlined. Also approximate analytical solutions valid for short times are derived.

5. Current-time curves for a particular small radius of sphere and cylinder are compared with the corresponding planar-electrode curves. The small sphere yields higher currents at a given time than does the plate. The curve for the cylinder lies between the other two.

6. The current at a small sphere approaches a constant value, different from zero, as $t \to \infty$. The long-time current permits determination of the charge-transfer parameters because the reaction remains under partial charge-transfer control at all times.

APPENDIX

Solution of the diffusion problem for spherical electrodes.

The diffusion equation for a system having full spherical symmetry is

$$D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r}) = \frac{\partial c}{\partial t}$$

where $c = c(r,t)$ is the concentration at time t and radial distance r. On making the substitution[11]

$$U(r,t) = r\ c(r,t)$$

the diffusion equation becomes

$$D \frac{\partial^2 U}{\partial r^2} = \frac{\partial U}{\partial t}$$

and, in terms of the new variable $U = rc$ can now be treated in much the same fashion as diffusion in a linear system. Thus in the present problem we define

$$U_R(r,t) = r\ c_R(r,t) \quad ; \quad U_0(r,t) = r\ c_0(r,t) \tag{A1}$$

which satisfy the differential equations

$$D_R \frac{\partial^2 U_0}{\partial r^2} = \frac{\partial U_0}{\partial t} \quad ; \quad D_0 \frac{\partial^2 U_0}{\partial r^2} = \frac{\partial U_0}{\partial t} \tag{A2}$$

with initial conditions, for a spherical electrode of radius a,

$$r \geq a : \quad U_R(r,t=o) = c_R^o\ r \quad ; \quad U_0(r,t=o) = c_0^o\ r \tag{A3}$$

and the boundary conditions:

$$r \rightarrow \infty: \quad U_R(r,t) \rightarrow c_R^o\ r, \quad U_0(r,t) \rightarrow c_0^o\ r \tag{A4}$$

The remaining condition is that for the electrode current. The current density is given (in terms of the electrode reaction) by eq 1, which in the present notation is

$$\frac{i(t)}{i_o} = \frac{\exp[(1-\beta)n\epsilon\eta]}{c_R^o\ a} U_R(\ r = a, t) - \frac{\exp[-\beta n\epsilon\eta]}{c_0^o\ a} U_0(\ r = a, t) \tag{A5}$$

and (in terms of the diffusion currents) by

$$i(t) = - nFD_R \left(\frac{\partial c_R}{\partial r}\right)_{r=a} = + nFD_R \left[\frac{1}{a} \left(\frac{\partial U_R}{\partial r}\right)_{r=a} - \frac{1}{a^2} U_R(a,t) \right]. \tag{A6}$$

and

$$i(t) = -nFD_0 \left(\frac{\partial c_0}{\partial r}\right)_{r=a} = -nFD_0 \left[\frac{1}{a} \left(\frac{\partial U_0}{\partial r}\right)_{r=a} - \frac{1}{a^2} U_0(a,t) \right] \tag{A7}$$

On combining eq A5 - A7 we find the conditions which must be satisfied on the electrode surface $r = a$:

$$\left(\frac{\partial U_O}{\partial r}\right)_{r=a} = + U_O(a,t)\left[\lambda_O + \frac{1}{a}\right] - U_R(a,t)\,\lambda_R\kappa$$

(A8)

$$\left(\frac{\partial U_R}{\partial r}\right)_{r=a} = - U_O(a,t)\frac{\lambda_O}{\kappa} + U_R(a,t)\left[\lambda_R + \frac{1}{a}\right]$$

with $\kappa = D_R/D_O$ and

$$\lambda_R = \frac{i_o\,\exp[(1-\beta)n\varepsilon\eta]}{nFD_R\,c_R^o} \;;\; \lambda_O = \frac{i_o\,\exp[-\beta n\varepsilon\eta]}{nFD_O\,c_O^o}$$

(A9)

as in the Gerischer-Vielstich notation[8]. In terms of the Laplace transforms

$$Y_O(r,s) = \int_o^\infty e^{-st}\,U_O(r,t)dt$$

$$Y_R(r,s) = \int_o^\infty e^{-st}\,U_R(r,t)dt$$

the differential equations A2 and initial conditions A3 become

$$D_R\frac{\partial^2 Y_R}{\partial r^2} = sY_R - c_R^o\,r \;\;\;\; D_O\frac{\partial^2 Y_R}{\partial r^2} = sY_O - c_O^o\,r$$

(A10)

The solution which satisfies the boundary conditions A4 is

$$Y_O(r,s) = \alpha(s)\,\exp[-\sqrt{s/D_O}\,r] + c_O^o\,r/s$$

(A11)

$$Y_R(r,s) = \beta(s)\,\exp[-\sqrt{s/D_R}\,r] + c_R^o\,r/s$$

where $\alpha(s)$ and $\beta(s)$ are determined by the simultaneous solution of eq A8:

$$\alpha(s) = \frac{[\lambda_R\,\kappa c_R^o - \lambda_O c_O^o][a\sqrt{sD_O} + \sqrt{D_O D_R}]\cdot\exp[a\sqrt{s/D_O}]}{s[s + \gamma'\sqrt{s} + \delta']}$$

(A12)

$$\beta(s) = \frac{[\lambda_O c_O^o/\kappa - \lambda_R c_R^o][a\sqrt{sD_R} + \sqrt{D_O D_R}]\cdot\exp[a\sqrt{s/D_R}]}{s[s + \gamma'\sqrt{s} + \delta']}$$

with

$$\gamma' = \lambda_R\sqrt{D_R} + \lambda_O\sqrt{D_O} + (\sqrt{D_O} + \sqrt{D_R})/a$$

(A13)

$$\delta' = \sqrt{D_O D_R}[1 + a(\lambda_R + \lambda_O)]/a^2$$

(A14)

Equations A11, with the values of $\alpha(s)$, $\beta(s)$ from eq A12, determine the Laplace transforms of the variables $U_O(r,t)$, $U_R(r,t)$ and hence the concentrations $c_O(r,t)$, $c_R(r,t)$.

We require the values of the concentrations at the phase boundary $r = a$ and the current as functions of the time. The current is most easily obtained by taking the Laplace transform of eq A7:

$$J(s) = -nFD_O \left[\frac{1}{a}\left(\frac{\partial Y_O}{\partial r} \right)_{r=a} - \frac{1}{a^2} Y_O(a,s) \right] \tag{A15}$$

with $Y_O(r,s)$ given by eq A11 and

$$J(s) = \int_0^\infty i(t)\, e^{-st}\, dt$$

The current and concentrations are now readily obtained by inversion of eq A15 and A11. To accomplish this we must first factor the common denominator of $\alpha(s)$, $\beta(s)$,

$$(s + \gamma' \sqrt{s} + \delta') = (\sqrt{s} + \xi)(\sqrt{s} + \mu)$$

$$\xi = \tfrac{1}{2}\left\{ \lambda + (\sqrt{D_O} + \sqrt{D_R})/a + \left[\lambda^2 + \left(\frac{\sqrt{D_O} - \sqrt{D_R}}{a} \right)^2 + \frac{2}{a}(\lambda_R\sqrt{D_R} - \lambda_O\sqrt{D_O})(\sqrt{D_R} - \sqrt{D_O}) \right]^{\frac{1}{2}} \right\}$$

$$\tag{A16}$$

$$\mu = \tfrac{1}{2}\left\{ \lambda + (\sqrt{D_O} + \sqrt{D_R})/a - \left[\lambda^2 + \left(\frac{\sqrt{D_O} - \sqrt{D_R}}{a} \right)^2 + \frac{2}{a}(\lambda_R\sqrt{D_R} - \lambda_O\sqrt{D_O})(\sqrt{D_R} - \sqrt{D_O}) \right]^{\frac{1}{2}} \right\}$$

with $\lambda = \lambda_O\sqrt{D_O} + \lambda_R\sqrt{D_R}$. These relations yield[11]

$$c_R = c_R^o - \frac{A}{\sqrt{\kappa}(\xi-\mu)} \left[\frac{\sqrt{D_O}}{a}\left(\frac{1}{\mu} - \frac{1}{\xi} \right) + \left(1 - \frac{\sqrt{D_O}}{a\mu} \right)\exp\mu^2 t\,\, \mathrm{erfc}\mu\sqrt{t} \right.$$

$$\left. - \left(1 - \frac{\sqrt{D_O}}{a\xi} \right)\exp\xi^2 t\,\, \mathrm{erfc}\xi\sqrt{t} \right] \tag{A17}$$

$$c_O = c_O^o + \frac{A}{\xi-\mu} \left[\frac{\sqrt{D_R}}{a}\left(\frac{1}{\mu} - \frac{1}{\xi} \right) + \left(1 - \frac{\sqrt{D_R}}{a\mu} \right)\exp\mu^2 t\,\, \mathrm{erfc}\mu\sqrt{t} \right.$$

$$\left. - \left(1 - \frac{\sqrt{D_R}}{a\xi} \right)\exp\xi^2 t\,\, \mathrm{erfc}\xi\sqrt{t} \right] \tag{A18}$$

$$\frac{i_{(t)}}{i_{(t=o)}} = \frac{1}{1 + a\lambda_R + a\lambda_O} + \frac{1}{\zeta - \mu} \left[\frac{(\sqrt{D_R} - a\zeta)(\sqrt{D_O} - a\zeta)}{a^2\zeta} \exp\zeta^2 t \, \text{erfc}\zeta\sqrt{t} \right.$$

$$\left. - \frac{(\sqrt{D_R} - a\mu)(\sqrt{D_O} - a\mu)}{a^2\mu} \exp\mu^2 t \, \text{erfc}\mu\sqrt{t} \right] \tag{A19}$$

where A is given by eq 9a. These equations reduce to the corresponding results for planar electrodes if a is large, i.e., $a \gg (\lambda_R + \lambda_O)^{-1}$.

<u>Approximate solution of the diffusion problem for cylindrical electrodes.</u>
The diffusion equations for the species O and R in a system having full cylindrical symmetry are

$$D_O \left[\frac{\partial^2 c_O}{\partial r^2} + \frac{1}{r}\frac{\partial c_O}{\partial r} \right] = \frac{\partial c_O}{\partial t}$$

$$\tag{A21}$$

$$D_R \left[\frac{\partial^2 c_R}{\partial r^2} + \frac{1}{r}\frac{\partial c_R}{\partial r} \right] = \frac{\partial c_R}{\partial t}$$

and are to be solved subject to the initial conditions

$$r \geq a : \quad c_R(r,t=o) = c_R^o \, , \quad c_O(r,t=o) = c_O^o \tag{A22}$$

and the boundary conditions

$$r \to \infty : \quad c_R(r,t) \to c_R^o \, , \quad c_O(r,t) \to c_O^o \tag{A23}$$

$$i(t) = nFD_R \left(\frac{\partial c_R}{\partial r} \right)_{r=a} = -nFD_O \left(\frac{\partial c_O}{\partial r} \right)_{r=a} \tag{A24}$$

The combination of eq 1 and A24 yields the conditions which must be satisfied on the electrode surface $r = a$:

$$\left(\frac{\partial c_O}{\partial r} \right)_{r=a} = \lambda_O c_O(a,t) - \lambda_R \kappa \, c_R(a,t)$$

$$\tag{A25}$$

$$\left(\frac{\partial c_R}{\partial r} \right)_{r=a} = -\frac{\lambda_O}{\kappa} c_O(a,t) + \lambda_R c_R(a,t)$$

In terms of the Laplace transforms

$$U_O(r,s) = \int_o^\infty c_O(r,t)e^{-st} \, dt$$

$$\tag{A26}$$

$$U_R(r,s) = \int_o^\infty c_R(r,t)e^{-st} \, dt$$

the differential equations A21 and initial conditions A22 become

$$D_O \left[\frac{\partial^2 U_O}{\partial r^2} + \frac{1}{r} \frac{\partial U_O}{\partial r} \right] = s\, U_O - c_O^o$$

$$D_R \left[\frac{\partial^2 U_R}{\partial r^2} + \frac{1}{r} \frac{\partial U_R}{\partial r} \right] = s\, U_R - c_R^o \qquad (A27)$$

The solution which satisfies the boundary conditions A23 is[11]

$$U_O(r,s) = \frac{c_O^o}{s} + \alpha(s) K_0(\sqrt{\tfrac{s}{D_O}}\, r)$$

$$U_R(r,s) = \frac{c_R^o}{s} + \beta(s) K_0(\sqrt{\tfrac{s}{D_O}}\, r) \qquad (A28)$$

where $K_0(x)$ is the modified Bessel function of the second kind of order zero. $\alpha(s)$ and $\beta(s)$ are determined by the simultaneous solution of eq A25:

$$\alpha(s) = \frac{K_1(\sqrt{\tfrac{s}{D_R}}\, a) \sqrt{D_O}[\lambda_R \kappa\, c_R^o - \lambda_O\, c_O^o]}{s[\sqrt{s}\, K_1(\sqrt{\tfrac{s}{D_O}}\, a) K_1(\sqrt{\tfrac{s}{D_R}}\, a) + \lambda_O\sqrt{D_O}\, K_0(\sqrt{\tfrac{s}{D_O}}\, a) K_1(\sqrt{\tfrac{s}{D_R}}\, a) + \lambda_R\sqrt{D_R}\, K_0(\sqrt{\tfrac{s}{D_R}}\, a) K_1(\sqrt{\tfrac{s}{D_O}}\, a)]}$$

$$\beta(s) = \qquad (A29)$$

$$\frac{K_1(\sqrt{\tfrac{s}{D_O}}\, a) \sqrt{D_R}[\lambda_O\, c_O^o/\kappa - \lambda_R\, c_R^o]}{s[\sqrt{s}\, K_1(\sqrt{\tfrac{s}{D_O}}\, a) K_1(\sqrt{\tfrac{s}{D_R}}\, a) + \lambda_O\sqrt{D_O}\, K_0(\sqrt{\tfrac{s}{D_O}}\, a) K_1(\sqrt{\tfrac{s}{D_R}}\, a) + \lambda_R\sqrt{D_R}\, K_0(\sqrt{\tfrac{s}{D_R}}\, a) K_1(\sqrt{\tfrac{s}{D_O}}\, a)]}$$

where $K_1(x) = -dK_0(x)/dx$ is the modified Bessel function of the second kind and of order 1.

Equations A28 together with the values of $\alpha(s)$ and $\beta(s)$ from eq A29, determine $U_O(r,s)$ and $U_R(r,s)$, the Laplace transforms of the concentrations $c_O(r,t)$, $c_R(r,t)$. From either of these expressions, together with eq A24, we obtain the Laplace transform, $J(s)$, of the current $i(t)$:

$$J(s) = \frac{i_{(t=o)}}{\sqrt{s} \left\{ \sqrt{s} + \lambda_O\sqrt{D_O} \left[K_0(\sqrt{\tfrac{s}{D_O}}\, a)/K_1(\sqrt{\tfrac{s}{D_O}}\, a) \right] + \lambda_R\sqrt{D_R} \left[K_0(\sqrt{\tfrac{s}{D_R}}\, a)/K_1(\sqrt{\tfrac{s}{D_R}}\, a) \right] \right\}} \qquad (A30)$$

Unfortunately the expressions for U_O, U_R and J cannot be inverted analytically to give c_O, c_R and i. A complete solution may be obtained, however, by numerical inversion of the Laplace transforms, following the method described by Papoulis[13]. We used this procedure for the specific cases discussed in the text. In addition, an approximate analytic solution has been derived. This is valid for times much shorter than the smallest of a^2/D_O, a^2/D_R, $a/\lambda\sqrt{D_R}$, $a/\lambda\sqrt{D_O}$ (i.e., times sufficiently short that the diffusion distance is small in comparison with the radius of the electrode). The approximate short-time solution for the current, $i(t)$, will be sketched; short-time approximate solutions for the concentrations are found in much the same way, and only the final expressions will be given.

The approximate solution for $i(t)$ is based on the fact that the behavior of $i(t)$ for small t is determined by the behavior of $J(s)$ for large s. For large s we have[11]

$$\frac{K_0(\sqrt{\frac{s}{D_O}}\,a)}{K_1(\sqrt{\frac{s}{D_O}}\,a)} \to 1 - \frac{\sqrt{D_O}}{2a\sqrt{s}} + \frac{3\,D_O}{8\,a^2 s} + O(s^{-\frac{3}{2}})$$

so that, as $s \to \infty$,

$$J(s) \to \frac{i_{(t=0)}}{s + \lambda\sqrt{s} - (\lambda_O D_O + \lambda_R D_R)/2a} \tag{A31}$$

On factoring the denominator of this equation, as in the above treatment of the spherical electrode, we obtain

$$\frac{i_{(t)}}{i_{(t=0)}} = \frac{1+\bar{\delta}}{2\bar{\delta}}\exp\left[\left(\frac{1+\bar{\delta}}{2}\right)^2\lambda^2 t\right]\text{erfc}\left[\frac{1+\bar{\delta}}{2}\lambda\sqrt{t}\right]$$

$$- \frac{1-\bar{\delta}}{2\bar{\delta}}\exp\left[\left(\frac{1-\bar{\delta}}{2}\right)^2\lambda^2 t\right]\text{erfc}\left[\frac{1-\bar{\delta}}{2}\lambda\sqrt{t}\right] \tag{A32}$$

where

$$\bar{\delta} = \left[1 + \frac{2(\lambda_R D_R + \lambda_O D_O)}{a\lambda^2}\right]^{-\frac{1}{2}}$$

This result may be simplified by introducing the approximation $\exp x^2\,\text{erfc}\,x \simeq 1 - 2\pi^{-\frac{1}{2}}x + x^2$, valid for $x \ll 1$, to obtain

$$\frac{i(t)}{i(t=o)} \simeq 1 - \frac{2}{\sqrt{\pi}} \lambda \sqrt{t} + \left(1 + \frac{\lambda_R D_R + \lambda_O D_O}{2a\lambda^2} \right) \lambda^2 t \tag{A33}$$

Similarly the concentrations at the electrode surface, for small t, are given by

$$c_R(a,t) \simeq c_R^o - \frac{i(t=o)}{nF\sqrt{D_R}} \left[\frac{2}{\sqrt{\pi}} \sqrt{t} - \left(1 + \frac{\sqrt{D_R}}{2a\lambda} \right) \lambda t \right] \tag{A34}$$

$$c_O(a,t) \simeq c_O^o + \frac{i(t=o)}{nF\sqrt{D_O}} \left[\frac{2}{\sqrt{\pi}} \sqrt{t} - \left(1 + \frac{\sqrt{D_O}}{2a\lambda} \right) \lambda t \right] \tag{A35}$$

For large cylindrical electrodes, such that a >> $(\lambda_R + \lambda_O)^{-1}$, these equations reduce to the corresponding results for planar electrodes.

References

1. H. Gerischer, Z. Elektrochem. 54, 362 (1950).
2. R. Parsons, Trans. Faraday Soc. 47, 1332 (1951).
3. S. Barnartt, Electrochimica Acta 11, 1531 (1966).
4. H. Gerischer, Z. Elektrochem. 55, 98 (1951).
5. W. Vielstich and P. Delahay, J. Amer. Chem. Soc. 79, 1874 (1957).
6. P. Delahay, Advances Electrochemistry Electrochemical Eng. 1, 233 (1961).
7. P. Delahay, "Double layer and electrode kinetics", Interscience Publishers, New York (1965).
8. H. Gerischer and W. Vielstich, Z. physik. Chem. (N.F.) 3, 16 (1955).
9. H. Gerischer, Z. Elektrochem. 54, 366 (1950).
10. S. Barnartt, to be published.
11. H. S. Carslaw and J. C. Jaeger, "Conduction of heat in solids", 2nd ed. Clarendon Press, Oxford (1959).
12. S. Barnartt, J. Phy. Chem. 70, 412 (1966).
13. A. Papoulis, Quarterly Appl. Math. 14, 405 (1957).
14. I. Shain, K. J. Martin and J. W. Ross, J. Phys. Chem. 65, 259 (1961).
15. P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience Publishers, New York, New York (1954).
16. A quantitative treatment of this decrease in precision with time was given recently by K. B. Oldham and R. A. Osteryoung, J. Electroanal. Chem. 11, 397 (1966). These authors also present a novel method of evaluating λ and $i_{(t=0)}$ from current measurements in the intermediate-time range. Their method differs significantly from ours in that it involves current measurements from tangents drawn to the experimental current-time curve.
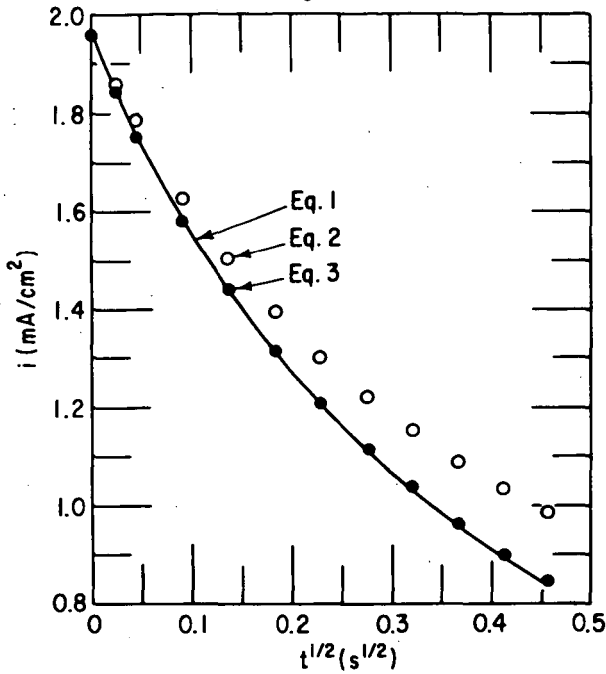
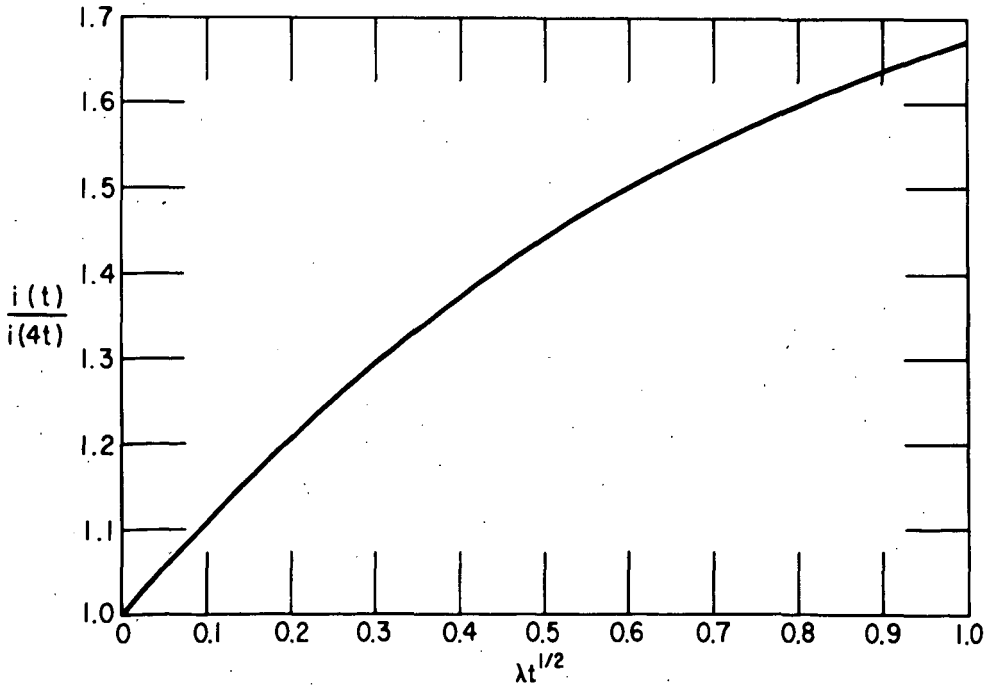FIG. I--CALCULATED CURRENT-TIME RELATIONS, PLANE ELECTRODES:
———Eq. I, ○Eq. 2, ●Eq. 3 .

FIG. 2-- VARIATION OF CURRENT RATIO $i_{(t)}/i_{(4t)}$ WITH $\lambda t^{1/2}$, PLANAR ELECTRODES.
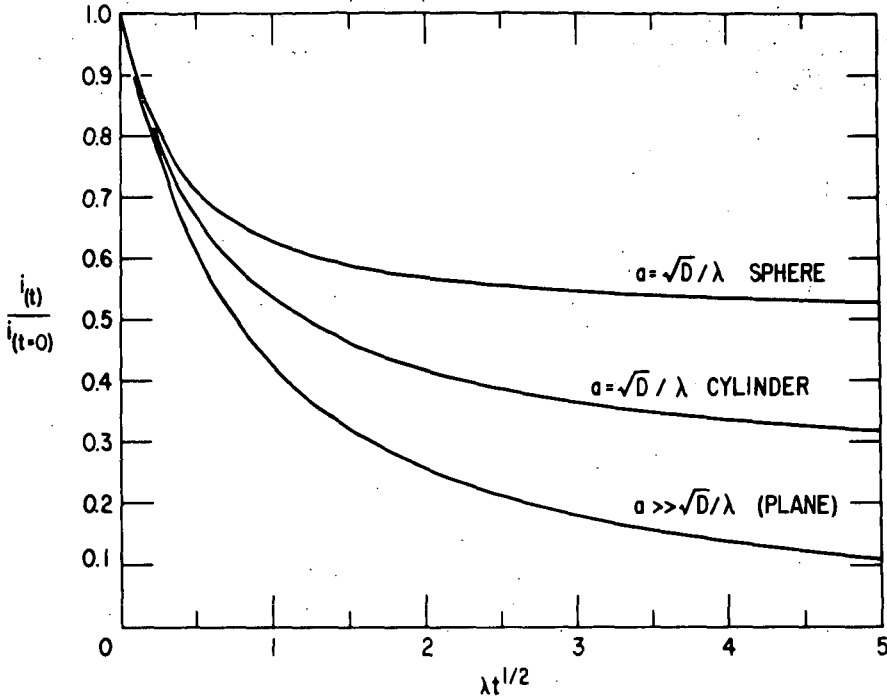
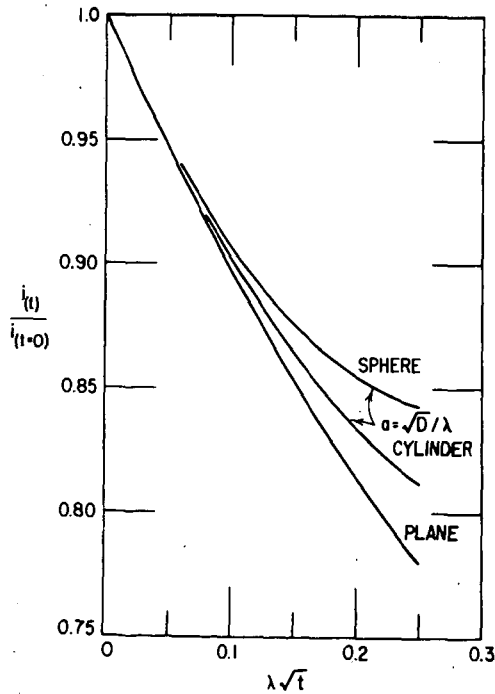FIG. 3-- CONSTANT-POTENTIAL CURRENT-TIME RELATIONS FOR SPHERICAL AND CYLINDRICAL ELECTRODES.

FIG. 4 -- CURRENT-TIME RELATIONS AT SHORT TIMES.